

2. TRACER TEST DESIGN FACTORS

Conducting quantitative tracing studies requires considerable knowledge of the tracer type employed, because simple measurement errors may occur as a result of tracer-specific effects, inappropriate sampling, and/or inappropriate analysis (Smart, 1988a). Smart and Laidlaw (1977) and other sections of this document discuss specific attributes of many of the fluorescent dyes commonly used for tracing ground-water flow. Field et al. (1995) provide a comprehensive discussion of the toxicity characteristics of several fluorescent dyes commonly used for tracing studies. Some typical fluorescent dyes used for tracing are listed in Table 1 and their structures shown in Figure 3.

Table 1. Some commonly used fluorescent dye types and their dye names with their respective Colour Index and CAS numbers.

Dye Type and Common Name	Colour Index Generic Name	CAS No.
<i>Xanthenes</i>		
sodium fluorescein	Acid Yellow 73	518-47-8
eosin	Acid Red 87	17372-87-1
<i>Rhodamines</i>		
Rhodamine B	Basic Violet 10	81-88-9
Rhodamine WT	Acid Red 388	37299-86-8
Sulpho Rhodamine G	Acid Red 50	5873-16-5
Sulpho Rhodamine B	Acid Red 52	3520-42-1
<i>Stilbenes</i>		
Tinopal CBS-X	Fluorescent Brightener 351	54351-85-8
Tinopal 5BM GX	Fluorescent Brightener 22	12224-01-0
Phorwite BBH Pure	Fluorescent Brightener 28	4404-43-7
Diphenyl Brilliant Flavine 7GFF	Direct Yellow 96	61725-08-4
<i>Functionalized Polycyclic Aromatic Hydrocarbons</i>		
Lissamine Flavine FF	Acid Yellow 7	2391-30-2
pyranine	Solvent Green 7	6358-69-6
amino G acid	—	86-65-7

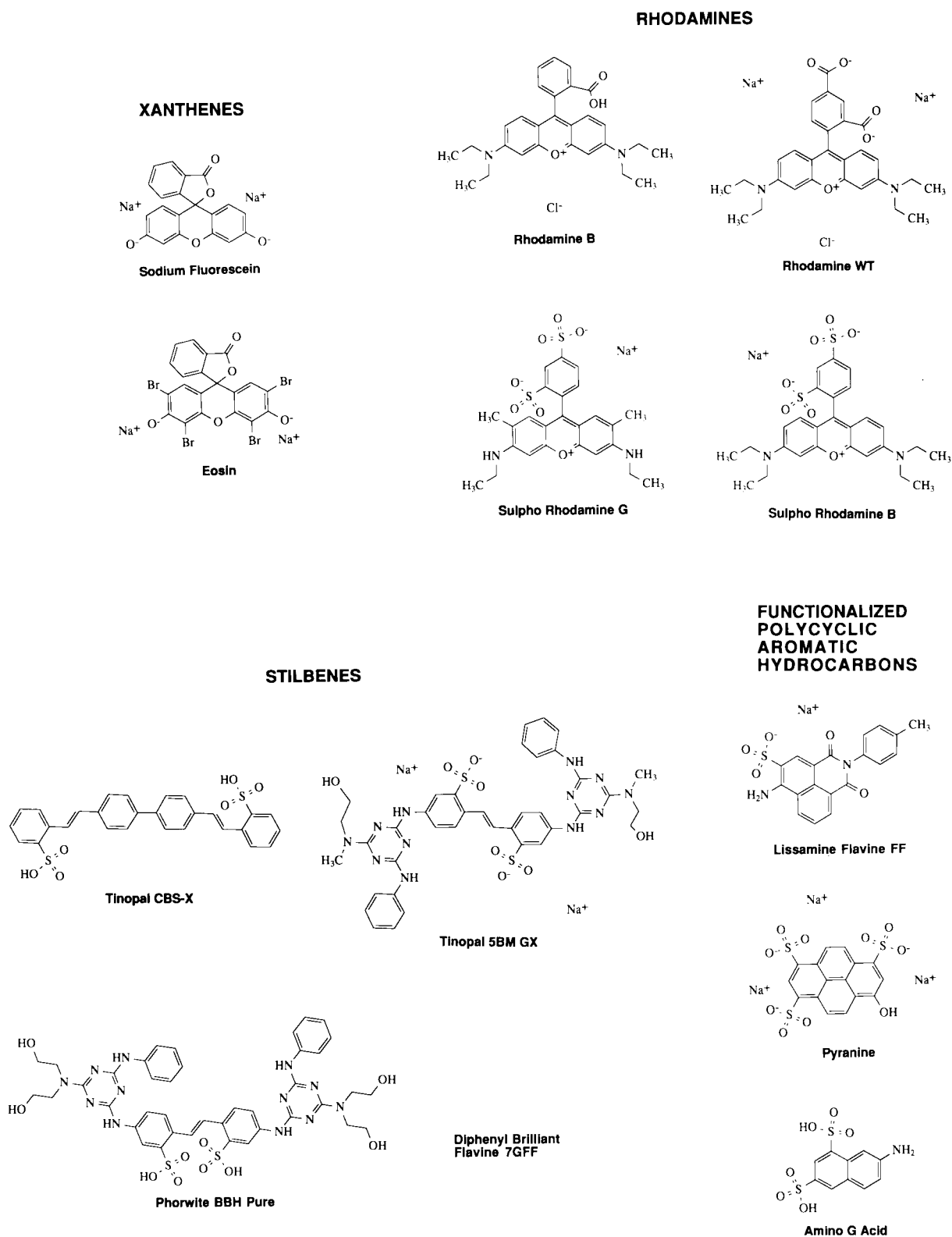


Figure 3. Chemical structures for selected fluorescent dyes used for water tracing.

Appropriate sampling efforts and frequencies for both tracer dye and ground-water discharge exert considerable influence on the accuracy of quantitative dye-tracing studies. Analytical methods must yield results with a high degree of precision as well. The fluorescent dyes listed in Table 1 fluoresce in the visible light spectrum anywhere from about 435 nm (Tinopal CBS-X) to approximately 584 nm (Sulpho Rhodamine B) (Table 2) (Figure 4).

Table 2. Data on some common fluorescent tracer dyes.

Dye Name	Maximum Excitation λ (nm)	Maximum Emission ¹ λ (nm)	Fluorescence Intensity (%)	Detection Limit ² ($\mu\text{g L}^{-1}$)	Sorption Tendency
sodium fluorescein	492	513	100	0.002	very low
eosin	515	535	18	0.01	low
Rhodamine B	555	582	60	0.006	strong
Rhodamine WT	558	583	25	0.006	moderate
Sulpho Rhodamine G	535	555	14	0.005	moderate
Sulpho Rhodamine B	560	584	30	0.007	moderate
Tinopal CBS-X	355	435	60	0.01	moderate
Phorwite BBH Pure	349	439	2	?	?
Diphenyl Brilliant	415	489	?	?	?
Flavine 7GFF					
Lissamine Flavine FF	422	512	1.6	?	?
pyranine	460 ³	512	18	?	?
	407 ⁴	512	6	?	?
amino G acid	359	459	1.0	?	?
sodium naphthionate	325	420	18	0.07	low

1. Values are approximate *only*. Different instruments will yield slightly different results.

2. Typical values for tracer detection in clean water using spectrofluorometric instrumentation.

Values may be adversely affected by augmented fluorescence and/or scattered light background.

Values will be lower when using filter fluorometric instrumentation.

3. $\text{pH} \geq 10$

4. $\text{pH} \leq 4.5$

Source: Behrens, 1986., Worthington, *pers. comm.*

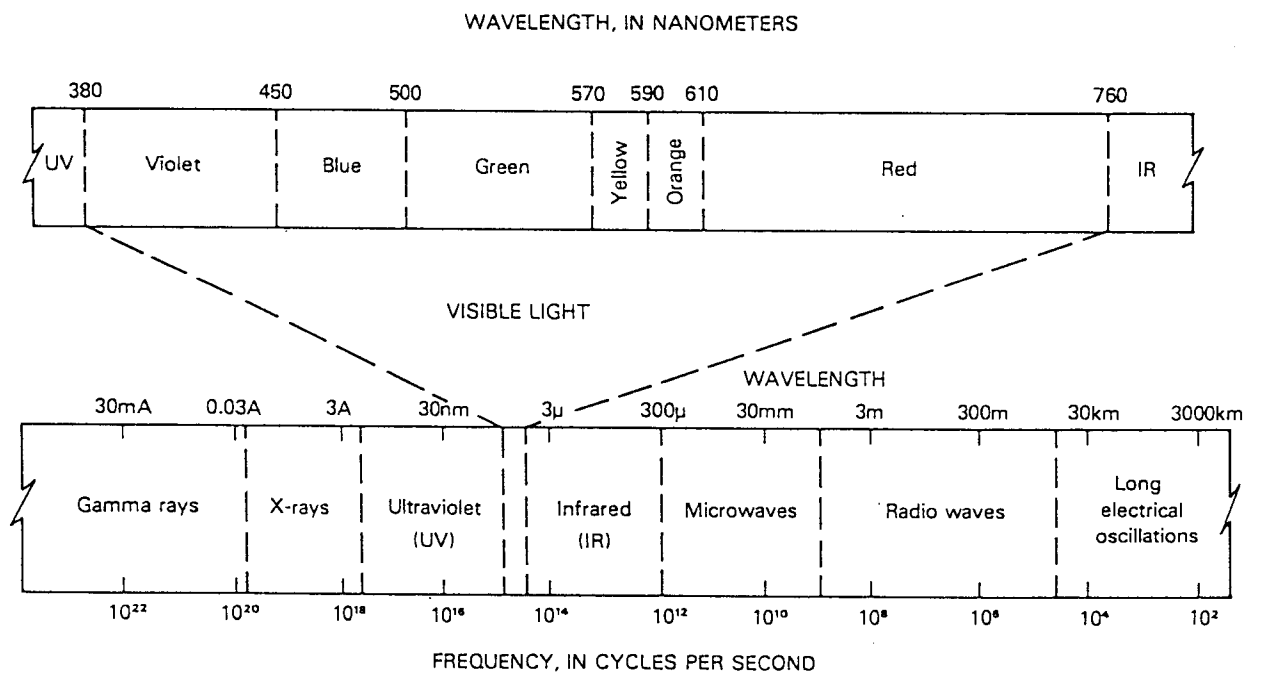


Figure 4. Electromagnetic spectrum with enlargement of visible spectrum for tracer dyes. Modified from Wilson et al. (1986, p. 3).

Lastly, different types of karst-conduit and fracture-flow networks will have a significant effect on tracer mass recovery, but such knowledge may be unknown to the tracing professional. These factors can be problematic when interpreting either qualitative or quantitative tracing study results and cannot be ignored.

2.1. TRACER CHARACTERISTICS

All chosen tracer substances should exhibit certain “ideal” characteristics, most notably conservative behavior. Unfortunately, no tracer substance is ideal, but fluorescent dyes are appropriate for tracing subsurface flow because of their low purchase cost, ease of use (injection, sampling, and analysis), low toxicity, relatively conservative behavior, high degree of accuracy of analysis, and low cost of analysis. However, specific aspects of any particular tracer dye chosen for a tracing study may adversely affect tracer recovery and thus lead to incorrectly calculated results (*e.g.*, mass-balance errors).

When conducting qualitative dye-tracing studies, it is usually sufficient to inject a known quantity of dye on an “as sold” basis which means that a considerable amount of diluent has been added to the dye (*i.e.*, < 100% dye). However, when conducting quantitative dye-tracing studies, the actual mass of dye injected into the aquifer must be known if the calculations are to be performed correctly.

Consider, for example, the commonly used fluorescent-tracer dye Rhodamine WT (Acid Red 388). For a qualitative trace, the tracing professional may decide to inject 18 pounds (2 gallons on an “as sold basis”) into the aquifer and be satisfied with the outcome. A quantitative trace would, however, require that the actual mass of the dye injected be calculated because Rhodamine WT is sold as a 20% solution (actually it is sold as a 17.5% solution, but is listed as a 20% solution) and because it has a density of 1.16 g cm⁻³. In this particular instance, the conversion to mass is developed from the following formula (Mull et al., 1988, p. 61):

$$V \times \rho \times \% = M_{in} \quad (1)$$

where V is volume [cm³], ρ is density [g cm⁻³], % is purity, and M_i is mass injected [g].

To determine the actual dye mass injected into the aquifer, the user must perform the following calculations:

1. Convert gallons to equivalent SI units (cubic centimeters for this example)

$$2.0 \text{ gal} \times 3.785 \times 10^{-3} = 7.570 \times 10^3 \text{ cm}^3$$

where 3.785×10^{-3} is a conversion factor.

2. Next insert the value obtained in step 1 into Equation (1)

$$\begin{aligned} 7.570 \times 10^3 \text{ cm}^3 \times 1.16 \text{ g cm}^{-3} \times 1.75 \times 10^{-1} &= 1.54 \times 10^3 \text{ g} \\ &= 1.54 \text{ kg} \end{aligned}$$

Subsequent quantification calculations would then use 1.54 kg for the mass of dye injected into the aquifer. Similar calculations for other tracer types need to be made using tracer-specific information.

Tracer sampling also presents some difficulty, depending upon the behavior of the tracer. All tracers will exhibit some loss due to sorption onto aquifer materials, but other factors may also cause a loss of tracer mass in the samples. For example, a commonly used dye for ground-water tracing, sodium fluorescein (Acid Yellow 73), tends to photodecay so that excess exposure to sunlight may diminish total mass recovery. Rhodamine WT is temperature dependent and requires correction of field measurements to a standard temperature. Even worse, it has recently been shown that Rhodamine WT naturally degrades to carboxylic fluorescein, which may substantially interfere with analyses and interpretations if sodium fluorescein was also used during the study (Gareth Davies, *pers. comm.*). Pyranine (Solvent Green 7) is *pH* dependent, which requires careful buffering of the water samples prior to analysis (Smart and Laidlaw, 1977).

2.2. TRACER INJECTION

Ground-water and surface-water tracing both require labeling or “tagging” the flowing water with some identifying substance (*i.e.*, *tracer*) for subsequent detection at some distant point. This can only be achieved by getting the tracer to mix with the water. For surface-water tracing, this is not difficult. However, labeling ground water with a tracer can be fairly involved.

Typically, for karst systems the tracer substance, usually a fluorescent dye, is injected directly into a sinkhole or sinking stream that is believed to be connected to the karst conduit system. Figure 5 depicts a reinforced sinkhole located at the RCA del Caribe Facility (Barceloneta, Puerto Rico) that was used for plant waste-water injection and for tracer injection. Although small in appearance, this is a substantial entry point for water and pollutants.



Figure 5. Reinforced sinkhole receiving plant waste water at the RCA del Caribe Facility. Waste water appears as clear water discharging from the rust colored pipe inside the sinkhole.



Figure 6. Dissolutionally enlarged fissure in limestone where most flow will occur. Precipitation of calcium carbonate in fractures appears as white and/or brown streaks.

Boreholes and wells are often used as injection points, but these are not as effective as sinkholes and sinking streams. Sinkholes and sinking streams are directly connected to the subsurface “plumbing” system of a karst aquifer. Boreholes and wells, in general, are rarely connected to the subsurface flow system.

Once injected, the tracer will move through the conduit system. Figure 6 depicts two fairly typical karst conduits that may exist in an area. From Figure 6 it is obvious that if the two conduits shown were at a depth of approximately 10–30 meters, it would be nearly impossible to detect them by any known geophysical means or to intersect them by a well. Monitoring wells are next to useless in this instance. However, a slug of tracer dye will use these conduits to migrate to a point where detection is possible.

2.2.1. Methods of Injection

Tracer injection can use a variety of methods. For example, it is not atypical to observe an injection in which a powder or liquid dye is injected (“dumped” and “introduced” are synonyms) directly into a sinkhole, sinking stream, or monitoring well. However, it is usually desirable to mix powder tracers with water prior to injection to prevent site contamination by air currents. The tracer/water mixture is then more easily poured into the injection point. Powder tracer mixing is most easily accomplished by adding a measured quantity of tracer into a large carboy (*e.g.*, 5 L) containing a small quantity of water (Figure 7).

After the preferred amount of tracer has been added to the carboy, more water is added to the mixture to bring the level up to about one-half to one-third full. The cap is then screwed down tightly and the carboy shaken vigorously to effect a thorough mixing. The carboy should be weighed before and after all additions and after injection so that a reasonably accurate estimate of tracer mass can be accomplished. The contents of the carboy are then easily released into the injection point (Figure 8).

Prior to tracer injection a substantial quantity of water (*e.g.*, 1000 gal.) should be released into the sinkhole or monitoring well (this is unnecessary for sinking streams). This “primer” of water helps to flush out the system of any debris and to lubricate the system. The tracer may then be added to the inflowing water. Alternatively, the water injection may be halted for tracer injection and then restarted after tracer injection.

A large quantity of chaser water (*e.g.*, 3000 gal.) is injected after tracer injection to help move the tracer along. Chase water helps to prevent the tracer getting stored in large dead-end pores and behind other obstructions. However, it is necessary in some instances (*e.g.*, monitoring wells) that care be taken not to raise the head excessively.

2.3. TRACER SAMPLING

Sampling for tracer must be performed in conjunction with discharge measurements for quantitative tracing because ground-water discharge and tracer-mass recovery are strongly interconnected. If discharge is not measured during the tracing study, but water samples are collected, then the tracing study may be considered semiquantitative. Sampling must also be of sufficient frequency so as to avoid the problem of aliasing (Smart, 1988a). Aliasing occurs when sampling frequencies are inadequate (*i.e.*, time intervals between individual sampling events are too far apart), which may cause certain aspects of tracer recovery to



Figure 7. Mixing fluorescein powder dye with water in a 5 L carboy. Fluorescein is a brick red color when a dry powder.



Figure 8. Injecting mixture of water and fluorescein dye into an injection well. Fluorescein has as a very dark red color when concentrated as shown here, but becomes a bright fluorescent green when diluted.

not be observed.

Additionally, cessation of sampling prior to complete recovery of the tracer mass may lead to an inadequate estimate of the aquifer characteristics desired. Field and Nash (1997) demonstrated the efficiency of numerical interpolation/extrapolation algorithms to fill gaps in the sampling data record.

2.4. SAMPLING EQUIPMENT

Mull et al. (1988, pp. 38–39) recommend that samples be collected by automatic samplers using glass sample bottles so as to minimize losses. Automatic samplers can be programmed to collect a water sample at appropriate sampling frequencies so that even midnight samples may be conveniently collected. Glass sample bottles are less likely to sorb the tracer than are plastic sample bottles, which may distort sample analysis results. Even if automatic samplers are not to be used, glass sample bottles are still appropriate for sample collection. The sample bottles need only be large enough to hold a maximum of approximately 32 mL of water in most instances.

Grab samples using appropriately sized test tubes with caps (*e.g.*, 25 mm × 150 mm) minimize handling. Samples should be stored tightly capped in a cool dark place. Shipping to the laboratory should be by cooler with an ice block enclosed.

Packets of activated charcoal may also need to be collected if fluorescent dyes are used as tracers. It is believed that activated charcoal will ensure dye recovery because the much lower dye concentrations found in water samples may not be detected in the water, or sampling frequencies may not have been adequate. The ability of activated charcoal to continue sorbing and concentrating fluorescent dye provides a sound means for determining fluorescent dye occurrence when water samples are ambiguous. However, at best activated charcoal will result in a qualitative tracing test only. More seriously, there is considerably more opportunity for sample contamination from handling. Still more serious is the recently considered problem of false positives and false negatives associated with activated charcoal packets.

2.5. SAMPLING LOCATIONS AND FREQUENCIES

Sampling locations and frequencies can be based on the results of qualitative dye-tracing studies so that appropriate sampling locations and frequencies may be determined in advance of conducting quantitative tracing studies. Preliminary qualitative tracing studies

may help ensure that proper sample collection will occur while minimizing expenses when quantitative tracing efforts are undertaken.

Should quantitative ground-water tracing efforts be initiated prior to qualitative tracing efforts, it is possible that too many or too few sampling locations will be utilized; the former drives up the cost while the latter results in incomplete tracer mass recovery. Sampling frequencies may also be inadequate, with the result being added costs (excessive number of samples collected) or inadequate tracer mass recovery (not enough samples collected often enough). Preliminary simple ground-water tracing studies can be useful for more difficult and complicated tracing studies. However, as previously discussed (Section 1.3.), recent studies have proven that with a basic understanding of the local hydrogeology and the use of automatic water sampling equipment, qualitative tracing efforts need not be conducted prior to quantitative tracing efforts.

2.6. TRACER MIXING IN THE CONDUIT

Complete lateral and vertical mixing of the tracer in a conduit or fracture(s) is considered ideal but not always possible. An acceptable mixing length is one in which the travel distance allows for nearly complete lateral mixing of the tracer and is considered to be an important factor in tracing surface-water flows (Kilpatrick and Cobb, 1985, pp. 2–3). Unfortunately, ground-water tracing in karst and fractured-rock aquifers does not always ensure that adequate lateral mixing will occur in karst conduits or fractures because tracing efforts are constrained to the limits of tracer-injection points as related to tracer-recovery points. Inadequate mixing may result in incorrect tracer-recovery calculations.

Mull et al. (1988, pp. 43–44) recommend that sampling during preliminary traces occur (at a minimum) at three places in the cross-section of spring and the tracer-breakthrough curves plotted for each sampling point in the cross-section. Complete lateral mixing is determined to have occurred when the areas under the tracer-breakthrough curves for each sampling location are the same regardless of curve shape or magnitude of the peaks; optimum results are obtained when mixing is about 95% complete (Figure 9) (Kilpatrick and Cobb, 1985, p. 3).

2.7. CORRECTION FOR BACKGROUND

All field measurements need to be corrected by subtracting background tracer concentrations from measured tracer concentrations. For example, sodium fluorescein is used to color automobile antifreeze. Because there are so many automobiles in existence and so many of

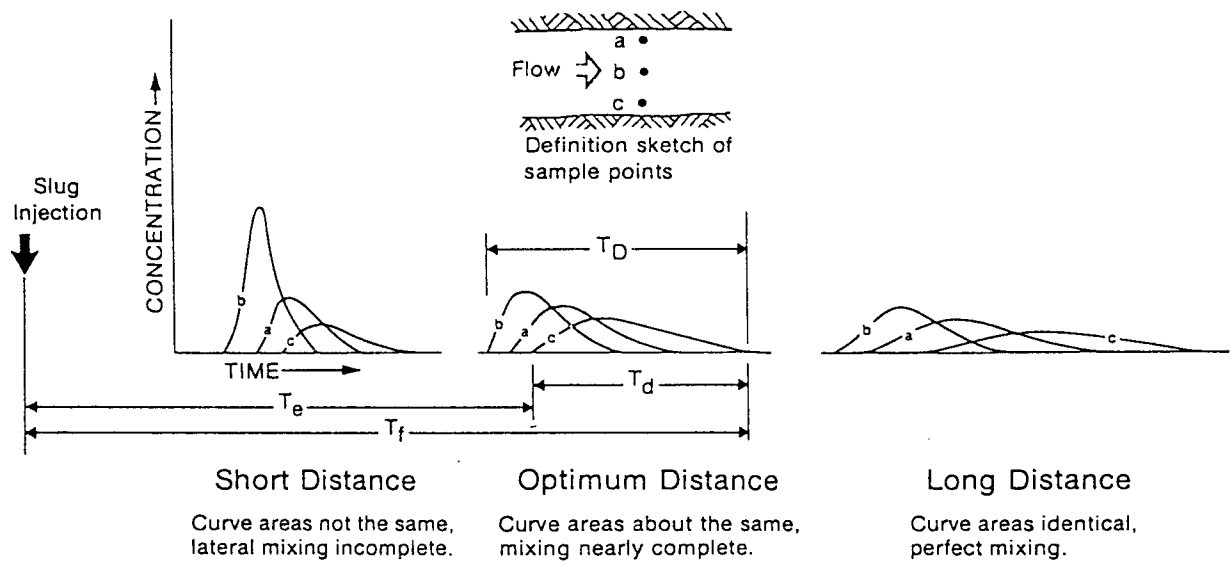


Figure 9. Typical response curves observed laterally and at different distances downstream from a slug injection of a tracer in the center of a stream (Kilpatrick and Cobb, 1985, p. 3).

them have leaks in their radiators, fluorescein-colored antifreeze is fairly ubiquitous in the environment.

Prior to any tracing efforts, background water samples need to be collected and analyzed for the tracer of interest. If the values obtained are low enough (*e.g.*, few $\mu\text{g L}^{-1}$), then the chosen tracer may be used; if not then a different tracer should be chosen. Low background concentrations in samples will then need to be averaged. This final value is then subtracted from every sample of recovered tracer from subsequent tracing efforts.

In addition, instrument calibration (*e.g.*, scanning spectrofluorophotometer and filter fluorometer) should be performed as described in the appropriate U.S. Geological Survey Techniques of Water-Resources Investigations publications (Kilpatrick and Cobb, 1985; Wilson et al., 1986). Proper instrument calibration is essential. Calibration using distilled water is common, but use of sample water is also acceptable.

2.8. DISCHARGE MEASUREMENTS

As stated previously, tracer sampling must be performed in conjunction with discharge measurements. If sampling is performed at wells that are being pumped at a constant rate, then discharge is fairly easily determined. Discharge at springs is considerably more difficult to estimate. If grab samples are being collected from nonpumping wells, then some estimate for flux past the well may need to be established.

Estimation of discharge may require special efforts on the part of the tracing professional. Weirs may need to be built, standpipes installed, flow meters utilized, and losses to evaporation estimated (for large bodies of water). Numerous documents describing methods for estimating discharge already exist, so the techniques will not be discussed here. Interested readers should examine the appropriate U.S. Geological Survey Techniques of Water-Resources Investigations publications for comprehensive discussion of discharge estimates.

Important to note is the possible occurrence of transient high-level overflows in which normally dry springs may discharge large quantities of water during storm events. Springs that are normally dry during low- to moderate-flow conditions may function during high-flow conditions. Efforts to address irregularly functioning springs should be prepared prior to initiating quantitative tracing studies so that discharge of tracer at such springs can be recovered.

Less common is the problem of sampling well screens set at elevations below which high-flow conditions occur. Such wells may be adequate for recovering tracer during low-

and moderate-flow conditions, but incapable of drawing in and discharging tracer during high-flow conditions. Presumably such an occurrence would be addressed by appropriate sampling at downgradient high-flow springs.

2.9. KARST CONDUIT NETWORKS

Tracing studies used in the determination of subsurface flow conditions in karst terranes are greatly influenced by various combinations of subsurface flow networks located between the inflow and outflow points of the aquifer. Seven types of karst networks are known to exist, as schematically shown on Figure 10.

The influence of karst networks on dye quantity present at a recovery site can be significant. If flow is through the simple Type I network, dye quantity estimates may be reasonably accurate. The more complex the karst network, however, the less likely it is that estimates of dye quantity will be adequate. As estimates become more difficult to make, it becomes tempting to use more dye than necessary. For Types II through VII (but excluding Type V), the estimate of dye quantity is likely to be low.

2.9.1. Network Types I, II, and III

If flow is through a Type I network, then predictions based on common tracing techniques may be reasonably accurate. If flow is through a Type II or Type III network, the accuracy of the predictions will tend to be inversely proportional to the amount of dye that is either diluted by additional water inflow or diverted to unknown discharge points. Distributary flow and multidirectional flow are subtypes of Types III and IV.

2.9.2. Network Types IV and V

Types IVa and IVb further complicate the flow determination because of significant loss of dye and because the identified outflow point will have a discharge rate that may be less than, greater than, or equal to the inflow point. Type V presents the worst situation related to flow prediction because no dye is recovered. This can lead to a false sense of a lack of hydraulic conductivity (*i.e.*, if the dye goes elsewhere, such results indicate there is no flow to the sites being monitored).

2.9.3. Network Types VI and VII

Types VI and VII are situations where either a significant amount of ground-water storage exists or a separate karst subsystem is connected to the main karst system. These are really

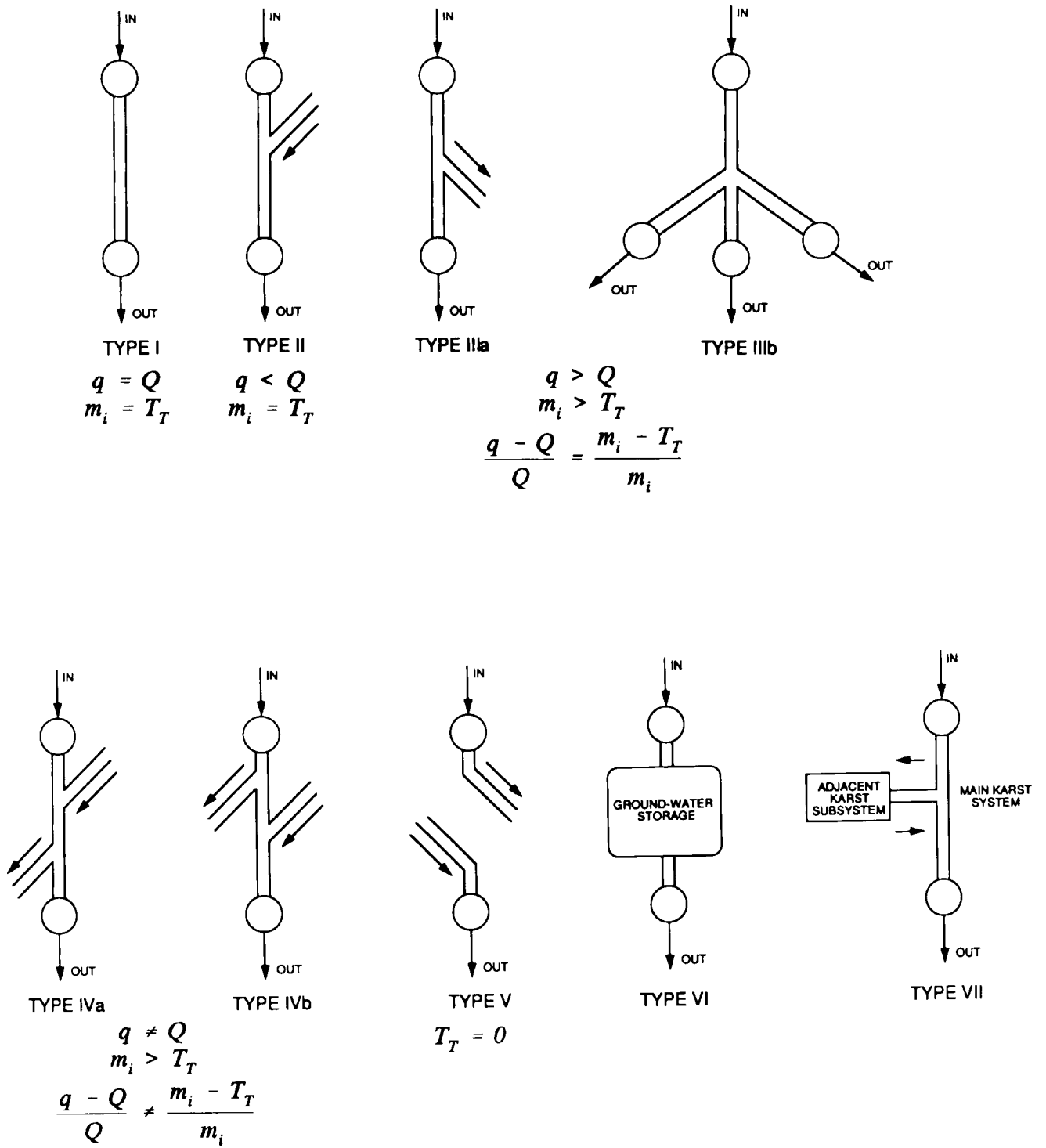


Figure 10. Seven simple karst network types that describe tracer migration in karst onduits. Any of these networks may significantly influence tracer tests between the point of inflow (IN) and the point of outflow (OUT) in a karst system. Discharge into the conduit is q , discharge out of the conduit is Q , tracer mass injected into the conduit is m_i , and tracer mass recovered is T_T . Note: Any one of these network types may be interconnected with any of the others. Modified from Atkinson et al. (1973) and Gaspar (1987b, p. 64).

subgroups of any one of Network Types I, II, III, IV, or V. As drawn, Network Types VI and VII appear only as subgroups of Network Type I, but additional inflows, outflows, or no connection to the sample-collection station(s) are realistic possibilities. For contaminant transport in a karst system, Network Types VI and VII may play significant roles.

2.10. DETERMINATION OF TOPOLOGICAL KARST CONDUIT NETWORK TYPE

Determination of the karst conduit network type usually requires extensive cave exploration, but can be roughly estimated from quantitative ground-water tracing studies. This is achieved by recognizing that each topological type exhibits specific characteristics that influence the results of tracing studies (Atkinson et al., 1973).

A Type I network (Figure 10) will exhibit such characteristics as inflow discharge equal to outflow discharge and mass of injected tracer equal to mass of recovered tracer

$$\begin{aligned} q &= Q \\ M_{in} &= M_{out} \end{aligned}$$

This assessment seems intuitively obvious considering that for both the inflow and outflow discharges to be equal and for complete tracer recovery to occur requires that a simple straight tube be defined. Other topological types become more difficult to assess as discharges and tracer recoveries become more complex (Figure 10).

It will be noted that Network Types VI and VII may fit into any one of the above categories, but with the added effect of storage in the system. Storage is not, however, accounted for in the simple relationships because it is only a delaying mechanism.